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(54) Title: PHOTOCURABLE RESIN COMPOSITION (57) Abstract A photocurable resin composition which comprises: (A) a urethane (meth)acrylate oligomer obtained by the reaction of (a) at least one polyol compound preferably selected from the group consisting of polyester polyols and polycarbonate polyols, (b) a polyisocyanate compound, and (c) a hydroxyl group-containing (meth)acrylate compound; (B) a (meth)acryloylphosphate; (C) a polyfunctional (meth)acrylate compound; and (D) a photopolymerization initiator. The composition exhibits a fast cure speed, and the cured products obtained from the composition exhibit superior adhesion under high temperature-high humidity conditions and metal corrosion properties.		

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PHOTOCURABLE RESIN COMPOSITION

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Field of the Invention

The present invention relates to a photocurable resin composition and, in particular, to a photocurable resin composition useful as an adhesive
10 for the manufacture of optical disks.

Background of the Invention

In recent years, development of high-density recording media has been pursued in response to the
15 demand for high capacity recording media, accompanied by advances in the quality of information such as letters, voice, picture images, and the like. An optical disk which is called a digital versatile disk (DVD) is one type of optical disk. A DVD can record a
20 greater amount of information than a CD (compact disk), even though these disks are almost the same in size. At present, DVDs are mainly manufactured by a so called bonding method, which comprises forming recording layers on at least one plastic disk by depositing metal
25 using a sputtering technique. The disks are then laminated together with an adhesive to form a mult-layer DVD.

A hot-melt type or a heat hardening type adhesive have been conventionally used in this method.
30 These adhesives, however, have exhibited problems in the length of time required for manufacturing optical disks. These adhesives not only require a long working time to obtain sufficient adhesion characteristics but also experience decreased adhesion under high
35 temperature-high humidity conditions, because these adhesives are easily softened and melted under such conditions. As a result, DVD disks bonded by

conventional adhesives have a tendency to become displaced when the optical disks are preserved under high temperature-high humidity conditions after manufacture, which is unacceptable.

5 To overcome these problems, ultraviolet radiation (UV) curable type adhesives comprising urethane acrylate as a major component have recently been proposed (for example, Japanese Patent Applications Laid-open No. 142545/1986, No. 10 89462/1994). However, these recently proposed adhesives much like the other conventional adhesives provide unsatisfactory photo-curability and adhesive properties.

 In addition, the use of these UV adhesives 15 have resulted in corrosion of the metal used in the recording layer because of moisture attack.

 An object of the present invention is to provide a photocurable resin composition possessing superior curability, producing cured products which 20 exhibit excellent adhesive properties under high temperature-high humidity conditions, and which are free from metal corrosion.

Summary of the Invention

25 As a result of extensive studies to solve these problems in the conventional techniques, the present inventors have found that these problems can be solved by a specific photocurable resin composition which comprises:

30 (A) an oligomer comprising a polymeric backbone, linked via urethane bonds to (meth)acrylate terminal groups (hereinafter referred to as a urethane (meth)acrylate (A)),

 (B) a phosphate containing at least one 35 (meth)acryloyl group (hereinafter referred to as (meth)acryloyl phosphate (B)),

 (C) a polyfunctional (meth)acrylate compound,

and

(D) a photopolymerization initiator.

Detailed description of the invention

5 The photocurable resin composition of the present invention will now be described in more detail.

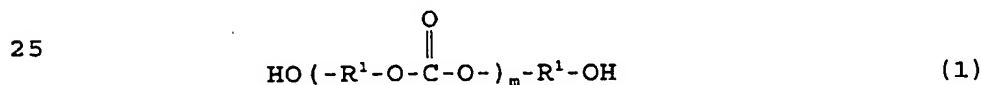
Urethane (meth)acrylate (A)

10 The urethane (meth)acrylate of component (A) comprises a polymeric backbone, urethane bonds and (meth)acrylate terminal groups. This oligomer containing an urethane bond preferably is obtained by condensation of (a) at least one polymeric polyol compound selected from a group consisting of polyester
15 polyols and polycarbonate polyols, (b) a polyisocyanate compound, and (c) a hydroxyl group-containing (meth)acrylate compound. The polyol compound constitutes the backbone, which is connected to the (meth)acrylate terminal groups through the urethane
20 groups that are formed by reaction of the isocyanates with the hydroxyl groups.

 The following compounds can be given as examples of the polyester polyols: polyester polyols obtained by the reaction of a polyhydric alcohol, such
25 as ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexane-dimethanol, 3-methyl-1,5-pentanediol, 1,9-nonanediol,
30 2-methyl-1,8-octanediol, or trimethylolpropane, and a dibasic acid, such as phthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, or sebacic acid; and polyester polyols obtained by reaction of ϵ -caprolactone, β -methyl- δ -valerolactone
35 or the like and the above-mentioned polyhydric alcohol. These polyester polyols may be used either individually or in combinations of two or more.

Given as commercially available products of these polyester polyols are Kurapol A-1010, 1510 and 2010, L-1010, 2010 and 3010, F-1010, 2010 and 3010, PNA-2000 and 2010, P-510, 1010, 1510, 2010, 3010 and 4010, PMIPA-2000, PKA-A, PKA-A2, MPD/IPA, MPD/TPA, CPM-1000 (manufactured by Kuraray Co., Ltd.); Nipporan 4002, 4009, 4010, 4032, 4040, 4042, 4060, 4070, 141, 143, 150, 5018, 5019, 5035 (manufactured by Nippon Polyurethane Industry CO., Ltd.); Adeka New Ace F15-20, F7-37, F18-62, F15-22, F7-68, F7-67, Y4-60, F13-35, F9-30, Y9-10, Y6-22, Y52-13, Y52-51, Y52-21, L4-71, V14-90, YG-108, YG-214, F1212-29, YG-226, Y96-20, YG-240, YT-101, YT-650, YT-651, YT-603, YT-400 (manufactured by Asahi Denka Kogyo Co., Ltd.); PLACCEL 205, 205AL, 212, 212AL, 220, 220AL, 303, 305, 308, 312, 320 (manufactured by Daicel Chemical Industries, Ltd.); and TONE 0301, 0305 and 0310 (manufactured by Union Carbide Corp.). Of these, Kurapol A-1010, 1510 and 2010, L-1010 and 2010, P-1010, 1510 and 2010, Adeka New Ace YG-108, YG-226, YG-240 and YG-214 are particularly desirable.

An example of useful polycarbonate polyols include those represented by the following formula (1):



wherein each R^1 independently represents usually an alkylene group having 2-20, preferably 4-15, carbon atoms, or a residual group (excluding the two hydroxyl groups) from (poly)ethylene glycol, (poly)propylene glycol, or (poly)tetramethylene glycol, wherein the plurality of R^1 's may be the same or different. And "m" denotes an integer from 1-30, preferably an integer from 3-20.

Given as specific examples of R^1 are residual groups, after exclusion of the two hydroxyl groups,

from 1,4-butanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, ethylene glycol, diethylene glycol, 5 triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, and tetrapropylene glycol.

Commercially available products of the polycarbonate diol include Nipporan 980, 981, 982, 983 10 (manufactured by Nippon Polyurethane Industry Co., Ltd.); PC-8000 (manufactured by PPG Industries, Inc.), PNOC1000, PNOC2000, PMC-100,2000 (manufactured by Kuraray Co., Ltd.); and PLACCEL CD-205, CD-208, CD-210, CD-220, CD-205PL, CD-208PL, CD-210PL, CD-220PL, CD- 15 205HL, CD-208HL, CD-210HL, CD-220HL, CD-210T, CD-221T (manufactured by Daicel Chemical Industries, Ltd.). Of these, PNOC1000, 2000, Nipporan 982, 983, PLACCEL CD-205HL, CD-210HL, and CD-220HL are particularly desirable.

20 The average number of hydroxy groups in the polyol generally will be between 1.8 and 4, preferable between about 2 and 3. Most preferably, the number of hydroxy groups of the polyol is about 2.

The number average molecular weight of the 25 polyol compounds measured by the terminal group method (OH-number, taking into account the functionality of the polymer polyol) is usually in the range of 200-20,000. To ensure adequate hardness and ease of handling of resulting adhesives, a molecular weight in 30 the range of 300-10,000, particularly 400-5,000, is preferred.

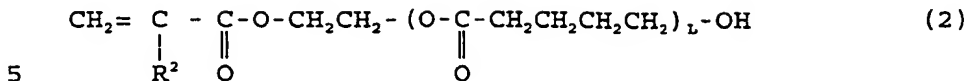
Examples of useful polyisocyanate compounds include diisocyanate compounds such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5- 35 naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-

diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl phenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, hydrogenated xylylene diisocyanate, hydrogenated diphenylmethane diisocyanate, methylenebis (4-cyclohexylisocyanate), 2,2,4-trimethylhexamethylene diisocyanate, 1,4-hexamethylene diisocyanate, and norbornane diisocyanate methyl. Lysine triisocyanate is given as an example of (useful) triisocyanate compound. Among the useful polyisocyanate compounds, 2,4-tolylene diisocyanate, isophorone diisocyanate, hydrogenated xylylene diisocyanate, and norbornane diisocyanate methyl are particularly desirable in view of reactivity of isocyanate groups, selectivity, and the characteristics of the resulting oligomers. These polyisocyanate compounds may be used either individually or in combinations of two or more.

The proportion of polyisocyanate compound used should be such that the isocyanate group contained in the polyisocyanate compound is usually 1-4 equivalents, preferably 1.1-3 equivalents, for one equivalent of the hydroxyl group contained in the above-mentioned polyol compound.

Given as examples of the hydroxyl group-containing (meth)acrylate compounds are 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, 2-hydroxy alkyl (meth)acryloyl phosphates (here, alkyl is methyl, ethyl, or propyl, for example), 4-hydroxycyclohexyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate; compounds shown by the following

formula (2),



wherein R^2 is a hydrogen atom or methyl group and L is an integer usually from 1-15, and preferably 1-4; and addition reaction products obtained from a glycidyl group-containing compound, such as alkyl glycidyl ether, allyl glycidyl ether, or glycidyl (meth)acrylate, and a (meth)acrylic acid. Of these compounds, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, and 2-hydroxy butyl (meth)acrylate are particularly desirable.

The amount of the hydroxyl group-containing (meth)acrylate compound used is such that the hydroxyl groups in the hydroxyl group-containing (meth)acrylate compound is usually 0.1-2 equivalents, preferably 0.1-1.5 equivalents, for one equivalent of the hydroxyl groups contained in the above polyol compound.

The following methods (I) to (III) are given as examples of methods for manufacturing the urethane (meth)acrylate (A). But, the methods are not necessarily limited to these.

(I) A method of reacting the polyisocyanate compound and a hydroxyl group-containing (meth)acrylate compound, and then reacting the polyol compound.

(II) A method of reacting the polyol compound, polyisocyanate compound, and hydroxyl group-containing (meth)acrylate compound all together.

(III) A method of reacting the polyol compound and polyisocyanate compound, and then reacting the hydroxyl group-containing (meth)acrylate compound.

Among these methods, the methods (I) and (III) are more desirable in view of the high probability of synthesizing the target oligomer and ease of manufacture.

The reaction temperature in these reactions is usually 10-90°C, and preferably 30-80°C.

The reactions (I)-(III) are preferably carried out in the presence of a urethanization catalyst, such as copper naphthenate, cobalt naphthenate, zinc naphthenate, di-n-butyl tin-dilaurate, triethylamine, 1,4-diaza-bicyclo[2.2.2]octane, or 1,4-diaza-2-methylbicyclo[2.2.2]octane. Typically, the catalysts are employed in an amount of 0.01-1 part by weight for 100 parts by weight of the total reactant.

The average functionality of the urethane (meth)acrylate (A) preferably is between about 1.8 and 8, more preferably lower than 4, and particularly preferred, about 2.

The urethane (meth)acrylate (A) typically has a number average molecular weight of 200-30,000. It has been found that urethane (meth)acrylates (A) having a number average molecular weight in the range of 400-20,000, particularly in the range of 600-10,000, provides photocurable resin compositions that are easier to handle and result in cured compositions having higher mechanical characteristics.

The amount of the component (A) to be incorporated into the resin composition is usually 1-94 wt%, and preferably 5-80 wt%, of the total amount of the resin composition. To ensure superior adhesive properties, an amount of 10-70 wt% is particularly preferred. If the amount of the component (A) is too small, adequate adhesive properties cannot be obtained in the substrates; if too large, on the other hand, the viscosity of the composition is increased so that it becomes difficult for the resin composition to be processed with ease.

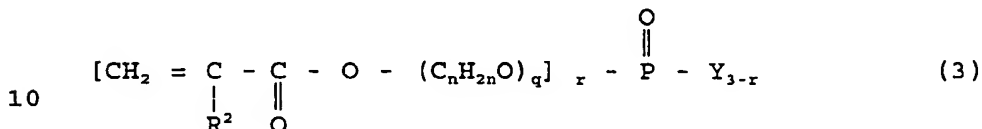
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(Meth)acryloylphosphite (B)

The (meth)acryloyl phosphates employed as

component (B) are phosphates possessing at least one, preferably one to three, (meth)acryloyl groups in one molecule. The compounds represented by the following general formula (3) can be given as examples of the

5 (meth)acryloyl phosphate (B).



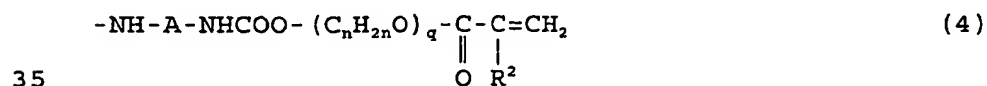
wherein R^2 has the same meaning as defined above; Y is a monovalent organic group.

15 Generally, Y, if present, represents an organic group with a molecular weight of about 1000 or less, preferably about 500 or less. The group Y may independently be alkyl, aryl and may comprise ether, amine, hydroxyl, urethane and ethylenically unsaturated

20 groups. Suitable examples of group Y are a group which possesses (1) at least one urethane bond (-NHCOO-) and a terminal (meth)acryloyl group, (2) a group represented by the formula, $-\text{OC}_a\text{H}_{2a+1}$, wherein a is an integer usually from 0-10, preferably 0-5, or (3) a

25 group represented by the formula, $-\text{OC}_6\text{H}_5$, provided a plurality of Ys may be the same or different. "n" is an integer from 1-10, preferably 1-5. "q" is an integer from 1-10, preferably 1-5. And "r" is an integer from 1-3, preferably 2-3.

30 A preferred example of Y includes groups represented by the following formula (4):



wherein n, q, and R^2 have the same meanings as defined above and A denotes a residual group excluding two -NCO groups from a diisocyanate compound.

40 Given as examples of the (meth)acryloyl

phosphate (B) include mono[2-(meth)acryloyloxyethyl]-
phosphate, di[2-(meth)acryloyloxyethyl]phosphate,
diphenyl-2-methacryloyloxyethyl phosphate, mono[2-
(meth)acryloyloxypolypropyloxy]phosphate, di[2-
5 (meth)acryloyloxypolypropyloxy]phosphate,
tris(acryloyloxyethyl)phosphate, and the compounds
represented by the above formula 3 wherein Y is
represented by formula (4), wherein A is the residual
group of toluene diisocyanate or isophorone
10 diisocyanate, and wherein "r" is 1 or 2. Preferably, in
formula (3), R² is methyl, whereas the R² in formula (4)
preferably is hydrogen.

These (meth)acryloyl phosphates (B) may be
used either individually or in combinations of two or
15 more.

The (meth)acryloyl phosphate (B) including
the monovalent organic group represented by formula
(4), may be prepared, for example, by condensing
compound of the general formula (3) (which contains at
20 least one -OH group bonded to a phosphorus atom,
hereinafter referred to as "(meth)acryloyl acidic
phosphate"), a diisocyanate compound, and a hydroxyl
group-containing (meth)acrylate compound.

Here, the same compounds given as examples in
25 the illustration of component (A), preferably 2,4-
tolylene diisocyanate and isophorone diisocyanate, are
given as the diisocyanate compound.

The amount of the diisocyanate compound used
is such that the amount of isocyanate groups contained
30 in the diisocyanate compound is usually 1-4, preferably
1.1-3, equivalents for one equivalent of the OH group
bonded to phosphorus atom in the (meth)acryloyl acidic
phosphate.

Also, the same compounds given as examples in
35 the illustration of the component (A), preferably 2-
hydroxyethyl (meth)acrylate and 2-hydroxypropyl
(meth)acrylate, are given as the hydroxyl group-

containing (meth)acrylate compounds used here.

The amount of the hydroxyl group-containing (meth)acrylate compound used is usually 0.1-3, preferably 0.5-2, equivalents for one equivalent of the OH group bonded to the phosphorus atom in the (meth)acryloyl acidic phosphate.

There are no specific limitations to the method for preparing the (meth)acryloyl phosphate (B) containing the group represented by formula (4). The following methods (i) to (iii) are given as typical examples.

(i) A method of reacting a diisocyanate compound and a hydroxyl group-containing (meth)acrylate compound, and then reacting a (meth)acryloyl acidic phosphate.

(ii) A method of reacting all three components together.

(iii) A method of reacting the (meth)acryloyl acidic phosphate and a diisocyanate compound, and then reacting the hydroxyl group-containing (meth)acrylate.

Among these, the method (i) is preferred.

In the reactions according to the methods (i)-(iii), an amine-type urethanization catalyst, such as triethylamine, 1,4-diazabicyclo[2.2.2]octane, or 1,4-diaza-2-methylbicyclo [2.2.2]octane, can preferably be used in an amount of 0.01-1 parts by weight for 100 parts by weight of the total reaction components.

The reaction temperature is usually 10-90°C, and preferably 30-80°C.

Further, given as examples of commercially available products which can be used as the component (B) are Light Ester P-M, and P-2M (manufactured by Kyoeisha Chemical Co., Ltd.), Viscoat 3PA (manufactured by Osaka Organic Chemical Industry, Ltd.), EB-169, EB-170, EB-3603, and R-DX63182 (manufactured by Daicel UCB Co., Ltd.), AR-100, MR-100, MR-200 and MR-260 (manufactured by Daihachi Chemical

Co., Ltd.), and JAMP-100, JAMP-514 and JPA-514 (manufactured by Johoku Chemical Co., Ltd.). Of these, Light Ester P-2M, AR-100, MR-260, JPA-514, and Viscoat 3PA are preferred, with Viscoat 3PA being particularly preferred.

Preferably, the (meth)acryloyl phosphate (B) has a molecular weight of 150-2000, more preferably 200-1500.

Preferably, the (meth)acryloyl phosphate (B) has, before mixing this compound with the other constituents of the adhesive composition, a low amount of free acid groups. Preferably, the acid number of compound (B) is lower than 50, more preferably lower than 25 and most preferred lower than 10. The acid number represent the number of KOH mg required to neutralize 100 g of the (meth)acryloylphosphate (B).

A (meth)acryloyl phosphate (B) having a higher acid number than required can be reacted with isocyanate compounds, epoxy compounds and the like to have the amount of phosphoric acid groups reduced. It is also possible to simply esterify the acid groups. Suitable reactants for reaction with the acidic phosphate include mono-isocyanates, acrylate group comprising isocyanate compounds, glycidyl acrylate, bisphenyldiglycidyl ether, propene-oxide, cyclohexene-oxide, derivatives therefrom and the like.

The amount of (meth)acryloyl phosphate (B) present in the resin composition should be sufficient to provide adequate adhesive properties, particularly adhesion properties with metal but not excessive so as to cause the cured product to experience increased water absorption and/or exhibit decreased adhesive properties under high temperature - high humidity conditions.

The amount of the (meth)acryloyl phosphate (B) incorporated in the resin composition of the present invention is usually 0.1-30 wt%, preferably

0.1-20 wt%, and particularly preferably 0.5-10 wt%.

Polyfunctional (meth)acrylate (C)

- The component (C) is a polyfunctional
- 5 (meth)acrylate having a plurality functional groups, and free of urethane and phosphate groups. With this component it is possible e.g. to adjust the viscosity, the cure speed of the photo-curable resin composition, and the hardness of the resulting cured products.
- 10 Given as specific example of the polyfunctional (meth)acrylate (C) are ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate,
- 15 diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polypropylene glycol
- 20 di(meth)acrylate, neopentyl glycol di(meth)acrylate, hydroxypivalic acid neopentyl glycol diacrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol (meth)acrylate, pentaerythritol tetra-(meth)acrylate, ditrimethylolpropane tetra(meth)-acrylate,
- 25 dipentaerythritol hexa(meth)acrylate, trimethylolpropane trioxyethyl (meth)acrylate, trimethylolpropane trioxypropyl (meth)acrylate, trimethylolpropane polyethyleneoxyethyl (meth)acrylate, trimethylolpropane polyethyleneoxypropyl
- 30 (meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl) isocyanurate di(meth)acrylate, ethoxylated bisphenol A di(meth)acrylate, ethoxylated bisphenol F di(meth)acrylate, propoxylated bisphenol A
- 35 di(meth)acrylate, propoxylated bisphenol F di(meth)-acrylate, tricyclodecanedimethanol di(meth)acrylate, bisphenol A epoxy di(meth)acrylate, and bisphenol F

epoxy di(meth)acrylate. These compounds may be used either individually or in combinations of two or more.

Commercially available products can also be used as the component (C). Examples which can be given include Yupimer UV SA1002 and SA2007 (manufactured by Mitsubishi Chemical Corp.), Viscoat #195, #215, #230, #260, #295, #300, #310, #312, #360, #400 and #700 (manufactured by Osaka Organic Chemical Industry, Ltd.), KAYARAD MANDA, DPHA, NPGDA, R-604, DPCA20, -30, -60, -120, HX-620, D-310 and D-330 (manufactured by Nippon Kayaku Co., Ltd.), Aronix M-210, M-215, M-220, M-270, M-310, M-315, M-325, M-350, M-360, M-400, M-450, M-6100, M-6500, M-7100, M-8030 and M-8530 (manufactured by Toagosei Co., Ltd.), 3EG-A, BP-4EA, BP-4PA, PE-3A, TMP-A, PE-4A (manufactured by Kyoeisha Chemical Co., Ltd.), VR-77, VR-60 and VR-90 (manufactured by Showa Highpolymer Co., Ltd.), and SR-355 (manufactured by Sartomer Co., Ltd.). Of these, KAYARAD MANDA, R-604, Viscoat #300, Viscoat #295, VR-77, VR-90, TMP-A, and PE-3A are preferred.

The molecular weight of the polyfunctional (meth)acrylate (C) is usually 100-3,000, and preferably 200-2,000.

Component (C) should be present in the resin composition in an amount sufficient to provide a cured product that is sufficiently hard to avoid gaps and/or displacement between laminated substrates joined by the cured product. On the other hand, the amount of component (C) present in the composition should not be too high so as to provide a cured product having inadequate adhesive properties.

The amount of the component (C) incorporated into the composition of the present invention is usually 5-85 wt%, preferably 10-80 wt%, and particularly preferably 15-70 wt%.

Photopolymerization initiator (D)

Photopolymerization initiators commonly used with conventional photocurable resin compositions can be used as component (D) in the present invention without specific restrictions. Such commonly used photo-initiators include 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl methyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanethone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholino-propanon-1, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, 2-benzyl-2-dimethylamino-1-(4-morpholino phenyl)-butanone-1 and bis(2,6-dimethoxy-benzoyl)-2,4,4-trimethylpentyl phosphine oxide.

Further, the following products are given as examples of commercially available photopolymerization initiator (D): Lucirin TPO and Lucirin LR8728 (manufactured by BASF), Irgacure 184, 907 and 369 and CGI-1700 and 1850 (manufactured by Ciba-Geigy Ltd.), Darocur 1116, 1173 and 4265 (manufactured by Merck Co.), Ubecryl P36 (manufactured by UCB Co.), and Kayacure ITX, QTX, DETX and BMS (manufactured by Nippon Kayaku Co., Ltd.). Of these photopolymerization initiators, Lucirin TPO, Irgacure 184 and 369, CGI-1850, Kayacure ITX and DETX are especially desirable.

These photopolymerization initiators may be used either individually or in combinations of two or more.

The amount of the component (D) used in the composition of the present invention is usually 0.1-15 wt%, preferably 0.5-10 wt%, and particularly preferably

1-5 wt%.

Other components

Besides the above-mentioned components (A) to
5 (D), various components such as a photopolymerization
accelerator, monofunctional (meth)acrylates, vinyl
compounds, and various additives can be incorporated
into the composition of the present invention as
necessary for the particular application.

10 The following compounds are given as examples
of photopolymerization accelerators. Triethylamine,
diethylamine, N-methyldiethanoleamine, ethanolamine, 4-
dimethylaminobenzoate, 4-methyldimethylaminobenzoate,
4-ethyldimethylaminobenzoate, and 4-isoamyldimethyl-
15 amino-benzoate. As commercially available products of
these photopolymerization accelerators, Ubecryl P102,
103, 104 and 105 (manufactured by UCB Co.), KAYACURE
DMBI and EPA (manufactured by Nippon Kayaku Co., Ltd.),
and the like are given. The photopolymerization
20 accelerators are added to the composition in an amount
usually of 0-10 wt%, and preferably 0-5 wt%.

Given as examples of the monofunctional
acrylates are 2-hydroxyethyl (meth)acrylate, 2-
hydroxypropyl (meth)acrylate, 2-hydroxy butyl
25 (meth)acrylate, methyl (meth)acrylate, ethyl
(meth)acrylate, propyl (meth)acrylate, isopropyl
(meth)acrylate, butyl (meth)acrylate, amyl
(meth)acrylate, isobutyl (meth)acrylate, t-butyl
(meth)acrylate, pentyl (meth)acrylate, isoamyl
30 (meth)acrylate, hexyl (meth)acrylate, heptyl
(meth)acrylate, octyl (meth)acrylate, iso-octyl
(meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl
(meth)acrylate, decyl (meth)acrylate, iso-decyl
(meth)acrylate, undecyl (meth)acrylate, dodecyl
35 (meth)acrylate, lauryl (meth)acrylate, octadecyl
(meth)acrylate, stearyl (meth)acrylate,
tetrahydrofurfuryl (meth)acrylate, butoxyethyl

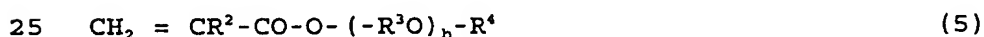
(meth)acrylate, ethoxydiethylene glycol (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, phenoxyethyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol

5 mono(meth)acrylate, methoxy ethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate, ethoxyethoxyethyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxy polypropylene glycol (meth)acrylate, dicyclopentadienyl (meth)acrylate,

10 dicyclopentenyl (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, tricyclodecanyl (meth)acrylate, isobornyl (meth)acrylate, bornyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 7-amino-3,7-dimethyloctyl

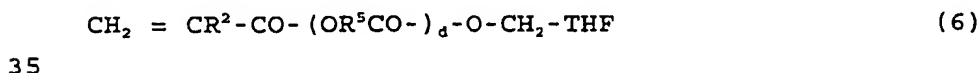
15 (meth)acrylate, (meth)acryloyl morpholine, 2-(meth)acryloyl- oxyethylphthalate, 2-(meth)acryloyloxyethylhexahydro-phthalate, 2-(meth)acryloyloxypropylphthalate, 2-(meth)acryloyloxypropyltetrahydrophthalate,

20 2-(meth)acryloyloxypropylhexahydrophthalate, 2-(meth)acryloyloxyethylsuccinate, acryloylmorpholine, the compounds represented by the following formulas (5) to (7):



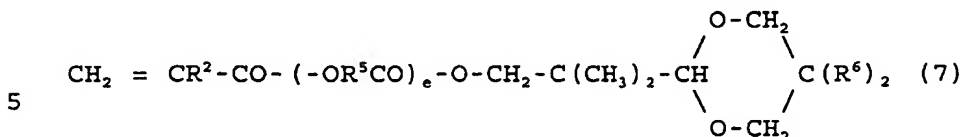
wherein R^2 has the same meaning as defined above, R^3 is an alkylene group having 2-6 carbon atoms, R^4 is an alkyl or aryl group having 1-25 carbon atoms, and is

30 preferably a phenyl group, optionally substituted with an alkyl group having 1-12 carbon atoms, and b is an integer from 0-12;



wherein R^2 has the same meaning defined above, R^5 is an alkylene group having 2-8 carbon atoms, THF is a

tetrahydrofuryl group and d is an integer from 0-8; and



wherein R^2 and R^5 have the same meanings as defined above, e is an integer from 0-8, and each R^6 independently is a hydrogen atom, an alkyl group having 1-6 carbon atoms, or the group represented by $-\text{R}^7 - \text{B}$, wherein R^7 is an alkylene group having 1-6 carbon atoms and B indicates a (meth)acryloyloxy group. These acrylates may be used either individually or in combinations of two or more.

Given as commercially available products of these acrylates are Aronix M-101, M-102, M-111, M-113, M-114, M-117, M-5300, M-5400, M-5500, M-5600, M110, TO-1317, TO-1301, TO-1249 and TO-1340 (manufactured by Toagosei Co., Ltd.), KAYARAD TC110S, R629 and R644 (manufactured by Nippon Kayaku Co., Ltd.), LA, STA, IBXA, DMA, Viscoat #158, #190, #192, #2000, #2100, #2150, #2180 and #3700 (manufactured by Osaka Organic Chemical Industry, Ltd.), NK Ester SA, and A-SA (manufactured by Shin-Nakamura Chemical Co., Ltd.), Light Acrylate L-A, S-A, BO-A, EC-A, DPM-A (manufactured by Kyoeisha Chemical Co., Ltd.) and FA-511A, FA-512A, FA-513A (manufactured by Hitachi Chemical Co., Ltd.), and ACO (manufactured by Kojin Co., Ltd.). Of these, IBXA, Viscoat #192, M110, TO-1317, FA-511A, FA-512A, FA-513A and ACO are particularly desirable.

N-vinyl caprolactam and N-vinyl pyrrolidone are given as examples of a preferred vinyl compound.

As various additives, silane coupling agents, antioxidants, UV absorbers, light stabilizers, aging preventives, polymerization inhibitors, preservatives, plasticizers, and the like are given.

Given as examples of silane coupling agents

are N-(2-aminoethyl)-3-aminopropylmethyl-
dimethoxysilane, N-(2-aminoethyl)-3-aminopropyl-
methylmethoxysilane, N-(2-amino ethyl)-3-amino-
propyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyl-
5 trimethoxysilane, 3-aminopropyltriethoxysilane, 3-
glycidoxypropyltrimethoxysilane, 3-glycidoxypropyl-
methyldimethoxysilane, 2-(3,4-epoxycyclohexyl)-
ethyltrimethoxy-silane, 3-chloropropylmethyl-
dimethoxysilane, 3-chloropropyl- trimethoxysilane, 3-
10 methacryloyloxypropyltrimethoxy-silane, and 3-
mercaptopropyltrimethoxysilane, and commercially
available products, such as Sails Ace S310, S311, S320,
S321, S330, S510, S520, S530, S610, S620, S710 and S810
(manufactured by Chisso Corp.), SH6020, SZ6023, SZ6030,
15 SH6040, SH6062, SH6076 and SZ6083 (manufactured by
Toray-Dow Corning Silicone Co.), and KBM403, KBM503,
KBM603, KBM602, KBM803 and KBE903 (manufactured by
Shin-Etsu Silicone Co., Ltd.)

As antioxidants, phenol-based antioxidants,
20 organic sulfur-based antioxidants, and commercially
available products, such as Irganox 1010, 1035, 1076
and 1222 (manufactured by Ciba-Geigy Ltd.), and the
like are given as examples.

As UV absorbers, benzotriazole-type UV
25 absorbers and the like can be given. As commercially
available products of the UV absorbers, Tinuvin P, 234,
320, 326, 327, 328 and 213 (manufactured by Ciba-Geigy
Ltd.), Sumisorb 110, 130, 140, 220, 250, 300, 320, 340,
350 and 400 (manufactured by Sumitomo Chemical
30 Industries Co., Ltd.), and the like are given as
examples.

As light stabilizers, hindered amine-type
light stabilizers are given. As commercially available
products of the light stabilizers, Tinuvin 292, 144,
35 622LD (manufactured by Ciba Geigy), Sanol LS-700, 765,
292, 2626, 1114 and 744 (manufactured by Sankyo Co.,
Ltd.), and the like are given as examples.

As examples of aging preventives, phenol-based aging preventives, allylamine-based aging preventives, and ketone amine-based aging preventives are given. Commercially available products of aging preventives include Antigen W, S, P, 3C, 6C, RD-G, FR and AW (manufactured by Sumitomo Chemical Industries Co., Ltd.).

These additives may be present in amount provided that the addition of these additives does not adversely affect the objects of the present invention. One of ordinary skill in the art, based on the particulars of the given application, the readily determine the amounts of a given additive to employ.

The composition of the present invention can be prepared by blending the above-described components by a conventional method. The resulting composition may have a viscosity of 20-20,000 mPa.s at 25°C. To ensure processability and ease of application to disk substrates, a viscosity in the range of 50-10,000 mPa.s at 25°C, particularly 100-2,000 mPa.s, is more desirable.

It is desirable that the various components are blended in proportions such that the glass transition temperature of the resulting cured products is in the range of 10-150°C, and preferably 30-120°C. If the glass transition temperature is too low, the cured products becomes so soft that substrates may be displaced when bonded; if the amount is excessive, on the other hand, sufficient adhesion cannot be obtained and substrates may bend.

Here, the glass transition temperature is defined to be the temperature at which the loss tangent ($\tan \delta$) is maximum at a vibration frequency of 10 Hz in a dynamic viscoelasticity measuring instrument.

The composition of the present invention can be cured by irradiating with ultraviolet light, visible rays, electron beams, or the like in the same manner as

conventional photocurable resin compositions are cured. For example, the composition may be applied to a substrate to make a film with a thickness of about 50 μm and can be substantially cured by irradiating with
5 ultraviolet light from a metal halide lamp with a dominant wavelength of 365 nm at a suitable dose. Generally a dose of less than 1000 mJ/cm^2 is sufficient, and the dose may be as low as 10 mJ/cm^2 . In practice, a dose of between 50-500 mJ/cm^2 often will be used to cure
10 the composition of the present invention.

It is desirable that the cured products have excellent transparency, for example, a cured product with a thickness of about 100 μm should have a transmittance of 90% or more at a wavelength of 500-600
15 nm. If the transmittance is less than 90%, not only the external appearance of the disks is impaired, but also there may be problems in reading the recording layer by laser beams. Therefore, when the composition of the present invention is manufactured, the various
20 components should be blended at proportions to provide a transmittance in this range.

In addition, the proportion of various components should be determined so as to make the refractive index of the cured products 1.50-1.60 at
25 25°C . If the refractive index is outside this range, errors may occur in reading the recording layer by laser beams.

The cured products of the composition of the present invention exhibit high adhesive properties to
30 substrates made of a plastic such as polycarbonate (PC) or polymethyl methacrylate (PMMA), a metal such as aluminum or gold, and an inorganic compound such as glass, and the like. The adhesion is excellent in a wide temperature range (for example $0-60^\circ\text{C}$) and is
35 stable under high temperature-high humidity conditions, indicating superior durability of the composition. Even when compositions of the present invention experience

water absorption as high as conventional adhesives, the corrosion exhibited by the adjacent metal substrate is slight or none.

Photocurable resin compositions of the present invention typically provide an adhesion property test value of greater than about 70, preferably 75-100 squares remaining. In particular, the photocurable resin composition of the present invention will provide at least about 90, preferably 95-100, squares remaining when tested on a PC substrate; greater than about 70, preferably 80-100, squares remaining when test on an Aluminium sputtered PC substrate; greater than about 70, preferably 75-100, squares remaining when tested on a gold sputtered PC substrate; and/or greater than about 90, preferably 95-100, squares remaining when tested on quartz substrate.

Photocurable resin composition of the present invention typically provide an adhesion property test value of greater than 50, preferably greater than 75, squares remaining when measured under high temperature - high humidity conditions and an aluminium sputtered PC substrate.

The photocurable resin compositions of the present invention should provide a light transmittance of less than about 50%, preferably less than 20%, when an aluminium sputtered PC board is exposed to high temperature - high humidity conditions in accordance with the Aluminium corrosion test set forth in the Examples.

Accordingly, the composition of the present invention is particularly useful as an adhesive for optical disks requiring high adhesive properties to plastics, metals, inorganic compounds, and the like.

35

EXAMPLES

The following examples of the present invention are presented for illustration purposes but

shall not be construed as limiting the present invention.

Synthesis of urethane acrylate (A)

5 Synthetic Example 1

23.0 g of isophorone diisocyanate, 69.0 g of PNOC1000 (trademark for polycarbonate diol manufactured by Kuraray Co., Ltd.), and 0.02 g of 2,6-di-t-butyl-methyl phenol as a polymerization inhibitor were fed
10 into a reaction vessel equipped with a stirrer. After cooling to 20°C or lower over a water bath, 0.08 g of di-n-butyl tin dilaurate was added to initiate the reaction. The mixture was reacted for two hours while controlling the temperature at 20-35°C. Then, after the
15 addition of 8.0 g of 2-hydroxyethyl acrylate, the mixture was stirred at 40-60°C for five hours, whereupon the reaction was terminated to obtain urethane acrylate (A-1) with a number average molecular weight of about 3,000.

20

Synthetic Example 2

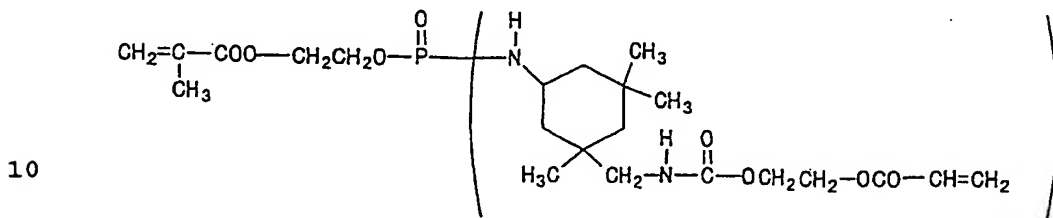
The same experiment as in Synthetic Example 1 was carried out except for using 69.0 g of Kurapol P1010 (a trademark of polyester diol manufactured by
25 Kuraray Co., Ltd.) instead of PNOC1000, to obtain urethane acrylate (A-2) with a number average molecular weight of 3,000.

Synthesis of methacryloyl phosphate (B)

30 Synthetic Example 3

To a reaction vessel equipped with a stirrer, 50.1 g of isophorone diisocyanate, 0.02 g of 2,6-di-t-butyl-methyl phenol as a polymerization inhibitor, and 0.08 g of di-n-butyl tin dilaurate were added. Then,
35 26.2 g of 2-hydroxyethyl acrylate was added dropwise and the mixture was reacted, while controlling the temperature to 30°C or lower over a water bath. Next,

23.7 g of mono(2-methacryloyloxyethyl) acidic phosphate and 0.1 g of triethylamine were added, and the mixture was reacted for five hours while stirring at 40-60°C. The reaction was terminated to obtain a compound with the following formula.



This compound is designated as methacryloyl phosphate (B-1) and served as a material to prepare the composition in Example 2.

Example 1

(1) Preparation of a photocurable resin composition

A vessel equipped with a stirrer was charged with 30.0 g of urethane acrylate (A-1), 29.0 g of isobornyl acrylate, 15.0 g of phenoxyethyl acrylate, 20.0 g of bisphenol A diepoxy acrylate, 2.0 g of tris(acryloyloxyethyl)phosphate as an acryloyl phosphate, 3.0 g of 1-hydroxycyclohexylphenyl ketone as a photopolymerization initiator, and 1.0 g of 3-mercaptopropyltrimethoxysilane as a silane coupling agent. The mixture was blended at 50-60°C to obtain the composition of the present invention. The viscosity of the composition was 600 mPa.s at 25°C.

(2) Preparation and evaluation of cured product

The following tests were carried out using the composition prepared in (1) above.

2.1 Adhesion property test

The composition prepared in (1) above was coated on to a polycarbonate (PC) board, an aluminum sputtered PC board, a gold sputtered PC board, and a

quartz substrate to produce a film with a thickness of 50 μm . The composition were irradiated with ultraviolet light (light source: metal halide lamp) at a dose of 50 mJ/cm^2 in a nitrogen atmosphere to obtain cured test specimens. The cross-cut test according to JIS D0202 was carried out using the cured test specimens, wherein the number of squares of cross-cut cured film left on the board without being peeled off was counted. The results are shown in Table 2. The total number of squares initially existing on the board was 100.

2.2 Adhesion characteristics under high temperature-high humidity conditions

Cured test specimens prepared in the same manner as in 2.1 above using the aluminum sputtered PC board were allowed to stand in a thermo-hygrostat at 70°C and 95% RH for 96 hours. Moisture on the test specimens was wiped off and the cross-cut test was carried in the same manner as in 2.1 above. The results are shown in Table 2.

2.3 Aluminum corrosion test

Cured test specimens prepared in the same manner as in 2.1 above using the aluminum sputtered PC board were allowed to stand in a thermo-hygrostat at 70°C and 95% RH for 96 hours. Then, transmittance of the test specimens at 500 nm was measured using a spectrophotometer manufactured by Hitachi, Ltd. Aluminum corrosiveness was evaluated as an increase in the transmittance accompanied by dissolution of aluminum due to corrosion. The results are shown in Table 2. The transmittance of the test specimens before the test is 0% because of the existence of the aluminum layer.

2.4 Water absorption

Water absorption of the cured films was

measured according to JIS K7209 using the cured test specimens (substrate: quartz glass) prepared in the same manner as in 2.1 above. The results are shown in Table 2.

5

2.5 Glass transition temperature

The glass transition temperature of the cured films was measured using a compulsory resonance vibration type dynamic viscoelasticity measuring instrument (manufactured by Orientech Co., Ltd.) using the cured test specimens (substrate: quartz glass) prepared in the same manner as in 2.1 above. The temperature at which the loss tangent ($\tan \delta$) is maximum at a vibration frequency of 10 Hz was measured. The results are shown in Table 2.

2.6 Transparency

One drop of the composition was placed between two sheets of slide glass with a thickness of 1 mm each to produce a film. The thickness of the cured film was adjusted to 1 mm using a spacer. The composition was irradiated with ultraviolet light at a dose of 50 mJ/cm² to obtain a cured test specimen. The transmittance of light with a wavelength of 500 nm or 600 nm of the cured test specimen was measured using the same spectrophotometer as the used in the above experiment. The results are shown in table 2.

Example 2

A composition of the present invention was prepared in the same manner as in Example 1, except that 2.0 g of methacryloyl phosphate (B-1) was used instead of 2.0 g of the tris(acryloyloxyethyl)-phosphate. The viscosity of the resulting composition was 600 mPa.s. The composition was evaluated in the same manner as Example 1. The results are shown in Table 2.

Example 3

A vessel equipped with a stirrer was charged with 30.0 g of urethane acrylate (A-2), 29.0 g of dicyclopentenyl acrylate, 15.0 g of phenoxyethyl
5 acrylate, 20.0 g of hydroxypivalic acid glycol diacrylate, as the polyfunctional acrylate, 2.0 g of tris(acryloyloxy ethyl)phosphate as an acryloyl phosphate, 3.0 g of 2,4,6-trimethylbenzoyl
10 diphenylphosphine oxide as a photopolymerization initiator, and 1.0 g of 3-methacryloyloxypropyl-trimethoxysilane as a silane coupling agent. The mixture was blended at 50-60°C to obtain a composition of the present invention. The viscosity of the
composition was 700 mPa.s. The composition was
15 evaluated in the same manner as in Example 1. The results are shown in Table 2.

Example 4

A composition of the present invention was
20 prepared in the same manner as in Example 3, except that 3.0 g of di(2-acryloyloxyethyl) phosphate was used instead of 2.0 g of the tris(acryloyloxyethyl) phosphate and the addition of the 3-methacryloyloxypropyl-trimethoxysilane was omitted. The
25 viscosity of the resulting composition was 700 mPa.s. The composition was evaluated in the same manner as in Example 1. The results are shown in Table 2.

Example 5

30 A composition of the present invention was prepared in the same manner as in Example 1, except that the amount of the urethane acrylate (A-1) was changed to 15.0 g and 15.0 g of urethane acrylate (A-2) was added. The viscosity of the resulting composition
35 was 700 mPa.s. The composition was evaluated in the same manner as in Example 1. The results are shown in Table 2.

Comparative Example 1

A vessel equipped with a stirrer was charged with 34.0 g of isobornyl acrylate, 20.0 g of phenoxyethyl acrylate, 40.0 g of bisphenol A diepoxy acrylate, 2.0 g of trisacryloyloxyethyl phosphate as an acryloyl group-containing phosphate, 3.0 g of 1-hydroxycyclohexylphenyl ketone as a photopolymerization initiator, and 1.0 g of 3-mercaptopropyltrimethoxysilane as a silane coupling agent. The mixture was blended at 50-60°C to obtain a composition of the present invention. The viscosity of the composition was 800 mPa.s. The composition was evaluated in the same manner as in Example 1. The results are shown in Table 2.

15

Comparative Example 2

A composition of the present invention was prepared in the same manner as in Example 1, except that the addition of trisacryloyloxyethyl phosphate was omitted and the amount of the bisphenol A diepoxy acrylate was changed from 20.0 g to 22.0 g. The viscosity of the resulting composition was 650 mPa.s. The composition was evaluated in the same manner as in Example 1. The results are shown in Table 2.

25

TABLE 1

		EXAMPLE					COMP. EXAMPLE	
		1	2	3	4	5	1	2
5	Components							
	(A) Urethane acrylate (A-1)	30.0	30.0	-	-	15.0	-	30.0
	Urethane acrylate (A-2)	-	-	30.0	30.0	15.0	-	-
	(B) Trisacryloyloxyethyl phosphate	2.0	-	2.0	-	2.0	2.0	-
	Di(2-acryloyloxyethyl) phosphate	-	-	-	3.0	-	-	-
	Methacryloyl phosphate (B)	-	2.0	-	-	-	-	-
10	(C) Bisphenol A diepoxy acrylate	20.0	20.0	-	-	20.0	40.0	22.0
	Hydroxyipivalic acid glycol diacrylate	-	-	20.0	20.0	-	-	-
	(D) 1-Hydroxycyclohexylphenyl ketone	3.0	3.0	-	-	3.0	3.0	3.0
15	2,4,6-Trimethylbenzoyl diphenylphosphine oxide	-	-	3.0	3.0	-	-	-
	Isobornyl acrylate	29.0	29.0	-	-	29.0	34.0	29.0
	Phenoxyethyl acrylate	15.0	15.0	15.0	15.0	15.0	20.0	15.0
	Dicyclopentenyl acrylate	-	-	29.0	29.0	-	-	-
20	3-Mercaptopropyltrimethoxysilane	1.0	1.0	-	-	1.0	1.0	1.0
	3-Methacryloyloxypropyltrimethoxysilane	-	-	1.0	-	-	-	-

TABLE 2

		EXAMPLE					COMP. EXAMPLE	
		1	2	3	4	5	1	2
5	Evaluation							
	. Adhesion properties (remaining)							
	PC substrate	100	100	100	100	100	10	90
	Aluminum sputtered PC substrate	100	100	100	90	100	70	5
	Gold sputtered PC substrate	100	100	80	75	100	70	5
10	Quartz substrate	90	100	95	90	100	90	90
	. Adhesion properties under high temperature-high humidity conditions ⁽¹⁾	95	100	95	80	95	10	0
	. Aluminum corrosion under high temperature-high humidity conditions ⁽²⁾	0	5	0	10	0	85	95
15	. Water absorption ⁽³⁾	1.7	2.0	1.9	2.3	1.8	1.2	1.8
	. Glass transition temperature (°C) ⁽³⁾	55	55	60	65	60	120	50
	. Transparency (%)							
	500 nm	99	98	94	94	98	98	98
20	600 nm	100	99	98	98	98	99	98

Note for Table 2

1) Substrate: Aluminum sputtered PC substrate

2) Substrate: Aluminum sputtered PC substrate

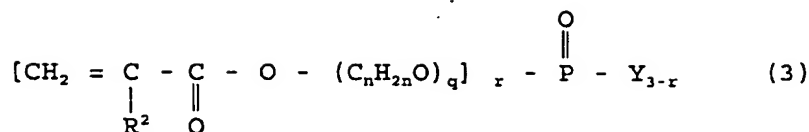
3) Substrate: Quartz substrate

Effects of the Invention

The photocurable resin composition of the present invention exhibits a faster cure speed than any conventional resin compositions on exposure to
5 radiation such as ultraviolet light, visible light, and electron beams. The cured product exhibits high adhesion to plastic substrates such as polycarbonate, metals such as aluminum or gold, or inorganic compounds such as glass. Moreover, the adhesion of the cured
10 product is excellent in a wide temperature range and stable even under high temperature-high humidity conditions. Although the cured product exhibits water absorption of the same level as conventional products, the resulting amount of corrosion of sputtered metal is
15 slight or none. The resin composition therefore is useful as an adhesive for optical disks, for example, particularly as an adhesive for manufacturing bonding-type optical disks such as digital-versatile-disks, in which high adhesion to plastics, metals, inorganic
20 compounds, and the like is required.

C L A I M S

1. A photocurable resin composition useful as an adhesive for optical disks comprising:
 - 5 A) an urethane (meth)acrylate oligomer,
 - B) a (meth)acryloyl phosphate,
 - C) a polyfunctional (meth)acrylate compound, and
 - D) a photopolymerization initiator.
- 10 2. The composition of claim 1, wherein the cured composition has a refractive index of about 1.50 to about 1.60 at 25°C.
3. The composition of claim 1, wherein the cured composition has a light transmittance of greater than 90% or more.
- 15 4. The composition of claim 1, wherein a 50 μ m thick layer of said composition is substantially cured upon exposure to UV light at a dose of from about 2 to about 50 mJ/cm².
5. The composition of claim 1, wherein the cured
20 composition has a glass transition temperature of between about 10 to about 500°C.
6. The composition of claim 1, wherein the cured composition has a glass transition temperature of between about 30 to about 120°C.
- 25 7. The composition of claim 1, wherein the composition has a viscosity in the range of about 100-2,000 mPa.s at 25°C.
8. The composition of claim 1, wherein the cured composition has an adhesion property test value,
30 when exposed to high temperature - high humidity conditions, of greater than 50 squares remaining.
9. The composition of claim 1, wherein the (meth)acryloyl phosphate comprises 2-3 (meth)acryloyl groups.
- 35 10. The composition of claim 1, wherein the (meth)acryloyl phosphate is represented by formula (3):



5

wherein

R² is a hydrogen atom or methyl group;

10 Y represents a monovalent organic group;

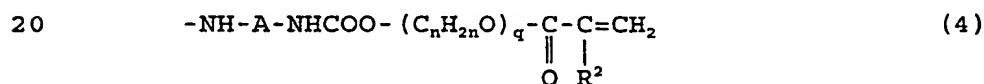
q is an integer from 1-10;

n is an integer from 1-10; and

r is an integer from 1-3.

11. The composition of claim 10, wherein Y represents
15 a monovalent organic group comprising at least one urethane bond and a terminal (meth)acryloyl group.

12. The composition of claim 10, wherein Y is represented by formula (4);



20

wherein

25 A represents a residual group excluding the two-NCO groups from a diisocyanate compound.

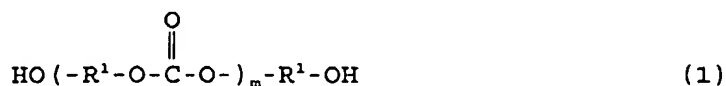
13. The composition of claim 12, wherein A is a residual group of toluene diisocyanate or isophorone diisocyanate.

30 14. The composition of claim 13, wherein r is 1 or 2.

15. The composition of claim 1, wherein the urethane (meth)acrylate oligomer has a polyester or polycarbonate backbone.

16. The composition of claim 1, wherein the urethane
35 (meth)acrylate oligomer is derived from a polycarbonate polyol represented by the formula (1):

40



wherein

each R¹ independently represents an alkylene group having 2-20, or a residual group, from

5 (poly)ethylene glycol, (poly)propylene glycol, or (poly)tetramethylene glycol; and m is an integer from 1-30.

17. The composition of claim 1, wherein the urethane (meth)acrylate oligomer is derived from 2-
10 hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate or 2-hydroxybutyl acrylate.
18. The composition of claim 1, wherein the urethane (meth)acrylate oligomer is obtained by an urethane reaction of
- 15 a) at least one polyol selected from a polyester polyol or a polycarbonate polyol,
b) a polyisocyanate compound, and
c) a (meth)acrylate compound.
19. An optical disk comprising a cured adhesive
20 composition comprised of:
A) an urethane (meth)acrylate oligomer,
B) a (meth)acryloyl phosphate, and
C) a polyfunctional (meth)acrylate compound.
20. A photocurable adhesive comprising
25 A) an urethane(meth)acrylate oligomer,
B) a (meth)acryloyl phosphate having an acid number lower than 50, and
C) a polyfunctional (meth)acrylate compound.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 98/00089

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G03F7/027 G11B7/24

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03F G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 094 329 A (HITACHI CHEMICAL COMPANY LTD.) 15 September 1982 see page 3, line 6 - line 13 see page 5, line 12 - line 35 see page 7; example 2 ---	1-10, 17, 20
A	DATABASE WPI Section Ch, Week 9417 Derwent Publications Ltd., London, GB; Class A89, AN 94-141483 XP002065891 & JP 06 089 462 A (TOKYO THREE BOND CO LTD) cited in the application see abstract --- -/-	1-20

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

26 May 1998

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INTERNATIONAL SEARCH REPORT

Intern nal Application No

PCT/NL 98/00089

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 175 035 A (SUMITOMO METAL INDUSTRIES, LTD.) 26 March 1986 see claims	1-18,20
A	US 4 738 870 A (J.G. GREEN ET AL.) 19 April 1988 see column 10; example 2	1-18,20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 98/00089

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